Agenda

- Study Approach
- Applied Methodology
- Results
- Outcomes
- Prospects
Study Approach

• Environmental regulations, market disruptions or economical strategies can induce changes in materials

• These changes can have a big industrial impact (reliability, planning, economic...) due to the need of re-qualifications

• The deep knowledge of materials composition and performances will allow space industries to be proactive in case of materials obsolescence, minimizing risk, cost and time

• Thus, it is crucial to:
  – identify their risk with respect to obsolescence
  – compare their compositions and properties (old/new formulations)
Applied Methodology

• Each selected product can be analyzed with various degrees of refinement depending on the needs for global or specific information:

  – **Level 1 / Global fingerprinting**
    Analysis of the bulk formulation without or with limited isolation

  – **Level 2 / Detailed analysis**
    Determination and quantification of the main ingredients in each formulation

  – **Level 3 / Precise quantification**
    Determination and quantification of minor compounds of interest or of concern

  ➔ Use of standard methods
  ➔ Development of specific analytical methods for determining the presence of a specific ingredient of interest and its precise content in the complex blend
Analytical Methods

- Experimental procedure and main characterization techniques

- Global strategy validated by implementing the sequence of steps on two families of products, namely epoxy adhesives and silicone elastomers

<table>
<thead>
<tr>
<th>Technique</th>
<th>Specific Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR (Fourier Transform IR Spectroscopy)</td>
<td>Identification of specific function, fingerprint</td>
</tr>
<tr>
<td>NMR (Nuclear Magnetic Resonance)</td>
<td>Structure identification and quantification $^1$H, $^{13}$C, $^{19}$F, $^{29}$Si</td>
</tr>
<tr>
<td>SEC (Size Exclusion Chromatography)</td>
<td>Molecular weight distribution</td>
</tr>
<tr>
<td>GC-MS (Gas Chromatography Mass Spectroscopy)</td>
<td>Volatile compounds analysis, identification of trace impurities</td>
</tr>
<tr>
<td>HPLC (High Performance Liquid Chromatography)</td>
<td>Non volatile organic analysis</td>
</tr>
</tbody>
</table>
Physical Testing

- Aim at determining potential evolution of the functional properties:
  - Mechanical
  - Thermo-Optical
  - Outgassing

<table>
<thead>
<tr>
<th>Technique</th>
<th>Specific Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lap-Shear</td>
<td>Determination of shear strength</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamical Mechanical properties</td>
</tr>
<tr>
<td>DSC</td>
<td>Phase Transitions</td>
</tr>
<tr>
<td>Outgassing</td>
<td>TML, RML, CVCM</td>
</tr>
</tbody>
</table>
Considered Materials

- Material list established to cover:
  - the widest panel of applications
  - different space industries (spacecraft, launchers, …)
  - sensitive constituents that could be soon impacted by regulations (Bisphenol A, …)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Nature</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesives/Tapes</td>
<td>Epoxy, Silicone, Acrylic, …</td>
<td>Structural, Multi-purpose, Electrical, …</td>
</tr>
<tr>
<td>Paints</td>
<td>Polyurethane</td>
<td>Thermo-optical</td>
</tr>
<tr>
<td>Varnishes</td>
<td>Silicone, Polyurethane, …</td>
<td>Electrical</td>
</tr>
<tr>
<td>Lubricants</td>
<td>Fluoropolymer</td>
<td>Mechanical</td>
</tr>
</tbody>
</table>
Level 1 / Fingerprinting:

- Typical analytical techniques: FTIR, $^1$H and $^{13}$C NMR
  - Fingerprinting of a polyurethane varnish (#P3)
  - FTIR spectrum of the hardener (polyol)
  - Simple way to control the relative intensity of the main bands assigned to the functional groups
Level 1 / Fingerprinting:

- Typical analytical techniques: FTIR, $^1$H and $^{13}$C NMR

  - Fingerprinting of a polyurethane varnish (#P3)

  - $^1$H NMR (600 MHz, CDCl$_3$, 8 scans, D1 = 15 s) analysis of the hardener

  - Much more informative, allowing for monitoring of possible evolutions in composition as a function of the production batch

  - Confirms the nature of the polyol, a castor-oil based triglyceride
Level 1 / Fingerprinting

- Typical analytical techniques: FTIR, $^1$H and $^{13}$C NMR
  - Fingerprinting of a polyurethane varnish (#P3)
  - $^{13}$C NMR (150 MHz, CDCl$_3$, 750 scans, D1 = 30 s) analysis of the hardener
  - Good sensitivity of the 600 MHz apparatus allows the detection of the presence of other fatty acids as minor constituents identified
Level 2 / Detailed Analysis

• Objective:
  Determination and quantification of the main ingredients in each formulation

• Comparison between a “new” commercial epoxy adhesive formulation and the previous one (“old”)

• Experimental steps:
  1. Fingerprinting (FTIR, NMR, HPLC or SEC)
  2. Collection of data from literature
  3. Analysis of model compounds
  4. Simulation of NMR spectra
  5. Addition of reference compounds
  6. Quantification
Level 2 / Detailed Analysis

- Several analyses performed to assess potential differences: **Epoxy Adhesives #E1/2**

- $^1$H and $^{13}$C NMR analysis for comparing the "new" formulation to the "old" one

- Globally, no significant differences: Similar composition for the old & the new formulations
Level 2 / Detailed Analysis

- Several analyses performed to assess potential differences: **Epoxy Adhesives #E1/2**

Resin
- NMR
- *Similar global composition of old & new formulations*
- *Main difference on the alkoxy silanes molar ratio*
  - 1% of GLYMO and traces of GLYEO in old formulation
  - 1% of GLYEO and traces of GLYMO in new formulation

![Chemical structures](image)

- Old - New
Level 2 / Detailed Analysis

- Several analyses performed to assess potential differences: **Epoxy Adhesives #E1/2**

**Resin**
- HPLC
  - *Only slight difference of the DGEBA oligomers content*
  - *standard deviation relative to 5 independent analyses much higher with the “new” formula*

<table>
<thead>
<tr>
<th>Old (5 samples)</th>
<th>New (5 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_t$ (min)</td>
<td>%-area</td>
</tr>
<tr>
<td>18.54</td>
<td>84.0</td>
</tr>
<tr>
<td>23.38</td>
<td>14.0</td>
</tr>
<tr>
<td>25.15</td>
<td>2.0</td>
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</tbody>
</table>
Level 2 / Detailed Analysis

- Several analyses performed to assess potential differences: Epoxy Adhesives #E1/2

Curing Mixture
- NMR
  - Same relative composition
  - No toluene detected in the new formulation

<table>
<thead>
<tr>
<th></th>
<th>OLD</th>
<th></th>
<th>NEW</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mw (g/mol)</td>
<td>molar %</td>
<td>wt. %</td>
<td>molar %</td>
</tr>
<tr>
<td>amide</td>
<td>969.5</td>
<td>34.6</td>
<td>68.4</td>
<td>35.7</td>
</tr>
<tr>
<td>DEGAE</td>
<td>220.31</td>
<td>21.9</td>
<td>9.8</td>
<td>21.4</td>
</tr>
<tr>
<td>DMP-30</td>
<td>265.39</td>
<td>32.5</td>
<td>17.6</td>
<td>32.5</td>
</tr>
<tr>
<td>BDMP</td>
<td>208.3</td>
<td>8.3</td>
<td>3.5</td>
<td>8.6</td>
</tr>
<tr>
<td>AEP</td>
<td>129.2</td>
<td>1.7</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>toluene</td>
<td>92.14</td>
<td>1</td>
<td>0.2</td>
<td>0</td>
</tr>
</tbody>
</table>

- $^1$H NMR stacking spectra
- $^{13}$C NMR stacking spectra
Level 2 / Detailed Analysis

• Several analyses performed to assess potential differences: **Epoxy Adhesives #E4/5**

**Resin**

– NMR
  – Similar composition of DGEBA oligomers
  – Presence of additives not detected

– HPLC
  – Slightly higher polymerization degree for the new formulation

<table>
<thead>
<tr>
<th>Old</th>
<th>New</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>0.15</td>
</tr>
<tr>
<td>(M_n)</td>
<td>384</td>
</tr>
<tr>
<td>EEW</td>
<td>192</td>
</tr>
</tbody>
</table>

\(n\): Polymerization Degree  
\(M_n\): Molecular Weight  
EEW: Epoxy Equivalent Weight

<table>
<thead>
<tr>
<th>DGEBA</th>
<th>(n=2)</th>
<th>(n=1)</th>
<th>(n=0) side products</th>
<th>(n=0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_t) (min)</td>
<td>24.1</td>
<td>24.9</td>
<td>25.8</td>
<td>26.5</td>
</tr>
<tr>
<td>Old</td>
<td>Average (%)</td>
<td>1.6</td>
<td>13.7</td>
<td>4.5</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>0.1</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>New</td>
<td>Average (%)</td>
<td>1.9</td>
<td>15</td>
<td>4.4</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.8</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Level 2 / Detailed Analysis

• Several characterizations performed to assess potential differences: Epoxy Adhesives E4/5

Curing Mixture

– NMR

– *No trace of aromatic solvent in the new formulation*

– *Same average amount of diamine in both formulations calculated from both $^1$H and $^{13}$C spectra*

• $^1$H NMR stacking spectra
  - aromatic solvent compound traces *only in old formulation*

• $^{13}$C NMR stacking spectra
Level 2 / Detailed Analysis

- Several characterizations performed to assess potential differences: **Mechanical Testing**

**Lap-shear test**

- *No significant impact of the formulation modification on the mechanical properties*

<table>
<thead>
<tr>
<th>Material</th>
<th>Average Failure Load (MPa)</th>
<th>Failure Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Old Formulation</td>
<td>New Formulation</td>
</tr>
<tr>
<td>Epoxy E1/2</td>
<td>32.7</td>
<td>30.8</td>
</tr>
<tr>
<td>Epoxy E4/5</td>
<td>20.3</td>
<td>21.1</td>
</tr>
</tbody>
</table>
**Level 3 / Precise Quantification**

- **Objective:**
  Demonstrate the feasibility and estimate the detection threshold for substances of concern in cured epoxy-based materials

- Quantifications of substance of concern, e.g. free bis-phenol A (BPA) and free bis-phenol F (BPF) in a cured epoxy sample

- **Experimental steps:**
  1. Establish a calibration curve for the 2 bis-phenols by HPLC
  2. Curing of representative commercial epoxy adhesives
  3. Perform Soxhlet extraction
  4. Determine the amount of BPA or BPF and the unreacted monomers in the extracts
Level 3 / Precise Quantification

- Establish a calibration curve of BPA and BPF based on HPLC with UV detection

- HPLC with UV detection: Calibration for BPA and BPF concentration

- Detection limit of ~ 0.15 ± 0.03 ppm of bisphenol in the analyzed solution

https://www.anses.fr/sites/default/files/styles/accueil_article/public/art_BPA3.png?itok=U7NDiXWF
Level 3 / Precise Quantification

- Use of Soxhlet extraction on cured epoxy adhesive (#E8) with optimized protocol
- Identification of the compounds by HPLC (based on the retention time of reference compounds)
- Quantification of remaining BPA in the cured epoxy (by the method of standard additions)

→ presence of unreacted epoxy monomers in the extracts
→ BPA concentration in the tested solution: 3.8 mg L⁻¹
→ 120 ppm of BPA in the cured test material
→ detected amount much higher than the threshold value
Outcomes & Prospects

- Material list selected to cover the most used industrial material in European space industry
- Specific analytical protocols developed in order to characterize accurately the material composition
- The analyses performed improve the overall knowledge on material composition
- Reference data now available in order to assess the potential impact in case of material reformulation
- Completion of the physical testing and synthesis of the obtained results
- Release of guidelines for a standardized methodology to characterize the materials
- Issue of recommendations in case of material obsolescence
- Building of a material database including all the results obtained in the frame of the study
Acknowledgements

- ICMR
  - Xavier Coqueret & Guillaume Ranoux
  - Agathe Martinez & Sylvie Lanthon

- ESA
  - Malgorzata Holynska & Thomas Rohr
Thank you